Progress Report No. 9

July 1, 1964 to December 31, 1964

Effect of Pressure on Metallurgical Phenomena

NASA Grant No. NsG-90-60

A. Transformations in the Alloy System Tl-Pb

I. Alloys

In order to better interpret any high pressure data on phase transformations in the Tl-Pb system, it was considered necessary to study the temperature vs composition diagram at atmospheric pressure, because of uncertainties in the diagram.

Twenty-six alloys in the range from 1-40 atomic percent lead were made and processed to 0.060 inch diameter wire, which is to be used in pressure and resistivity experiments.

It is necessary to store each alloy in a vial of ethelene glycol. In order to prevent the solution of thallium into the ethelene glycol, the samples are kept at dry ice temperatures.

II. Resistivity Measurements

The method chosen for the determination of the atmospheric pressure diagram was the measuring of resistivity as a function of temperature.

The 0.060 inch diameter sample of alloy wire must be drawn to a diameter of 0.038 inches for use in the resistivity apparatus.

Resistance is determined by measurement of voltage drops across the thallium alloy and across a known resistance. To provide a protective atmosphere for the thallium alloys, they are heated in a bath of canthus-210 oil. Resistivity is measured on both heating and cooling, and the rates of both processes are controlled as desired. Runs of 0-6 atomic % Pb have been made.

III. Results

Pure thallium is stable as h.c.p. α up to 234°C. At this temperature an allotropic transformation occurs to form a body-centered-cubic beta structure.

The effect of lead additions is to lower the temperature of the transformation. Our results suggest a eutectoid reaction at about 180°C and a eutectoid composition of 4.2 atomic % Pb. This is about 40°C higher and 1 atomic % less Pb than determined by Guertler and Schulze.(1)

Cooled β alloys were found to supercool large amounts, up to 100°C. This indicates that the b.c.c. phase, which is metastable with respect to the alpha phase at room temperature, may be retained on quenching.

A lesser degree of supercooling was found in the Tl-In system by other investigators. The b.c.c. phase was retained in this system by quenching under pressure.

IV. X-Ray Diffraction

A high temperature X-ray diffraction unit will be used to take X-ray diffraction patterns of the thallium-lead alloys at various temperatures. The equipment is now being calibrated in the temperature range of room temperature to about 250°C. The

(1) W. Guertler and A. Schulze, Z. Physik. Chem., No. 104, 1923, p. 269-309

temperature will be known to ± 2.5°C, instead of ±10°C, its present precision.

This equipment will soon be ready for use.

Section B. Irving B. Cadoff

THE EFFECT OF HIGH PRESSURE ON PbTe, SnTe AND PbxSni-xTe

The resistivity and Seebeck coefficient were measured as a function of temperature at different pressures. Temperatures were varied by utilizing double concentric graphite furnaces. There were shorts developed at high pressures between the leads of the two furnaces and between the leads of the inside furnace and the thermocouple wires. Due to the shorting, the results do not span the full pressure range of our machine. Log ρ vs $\frac{1}{T}$ at various pressures were plotted as shown in Fig. 1 and 2. The energy gap, Eg, of PbTe is obtained by measuring the slope of the intrinsic part of the curve at that particular pressure. Eg vs pressure is also plotted in Fig. 3. Although the two PbTe specimens did not show complete agreement, they both showed bends in the curve which is indicative of a second band entering the conduction process. Further work will be done on both p and n type PbTe and full range of pressure will be covered.

Due to the electric shorting problem at high pressures (as mentioned above) the design has been modified by using one cylindrical furnace. A temperature gradient is spontaneously developed between two ends of the furnace due to the non-uniformity of the machined graphite cylindrical wall. These newly designed cells were used on SnTe specimens and hence the full pressure range could now be covered. Similar tests of resistivity vs temperatures at different pressure were performed on SnTe. Results are shown in Fig. 4 and 5. At room pressure, the energy gap of SnTe was not measurable due to swamping by extrinsic carriers; but at high pressures $\log \rho$ vs $\frac{1}{T}$ plots show the exhaustion region and intrinsic region. The Eg was then measured from the slope of the intrinsic region and Eg vs pressure were plotted on Fig. 6. The $^{dEg}/_{dP}$ is positive (unlike PbTe) and therefore similar to most semiconducting materials. The Eg measured for the SnTe in conjunction with the resistivity measurements as explained below appears to indicate the presence of a third solid phase which was not reported by Kafalas*. The resistance of the Kafalas high pressure phase was 3.6 times higher than the room pressure phase as reported in his data. On similar tests (ρ vs pressure at room temperature) we observed a change by a factor of 5 which is roughly agreeable to Kafalas. Comparing this to our other results from the plot of $\log \rho$ vs $\frac{1}{T}$, at room temperature the resistance at high pressure is 17 times higher than that at room pressure, indicating that a third solid phase may exist at higher pressures and higher temperatures. Further work will be performed to determine the range of existence of the third phase.

* J. A. Kafalas and A. N. Mariano, High Pressure Phase Transition in SnTe. Science, Feb. 28, 1964., Vol. 143., No. 3609., P. 952.

APPENDIX I

Expenditures

1 July 1964 to 31 December 1964

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NASA Grant No. NsG-90-60

Salaries, Professional	- $ 2,310
Salaries, Research	- 10,967
Salaries, Graduate Students	- 4,212
Salaries, Clerical	- 2,481
Supplies	- 2,912
Miscellaneous (Social Security, Tuition Remission, Accrued Vacation, Travel)	- 2,878
Overhead (20%)	- 5,152
	$30,912

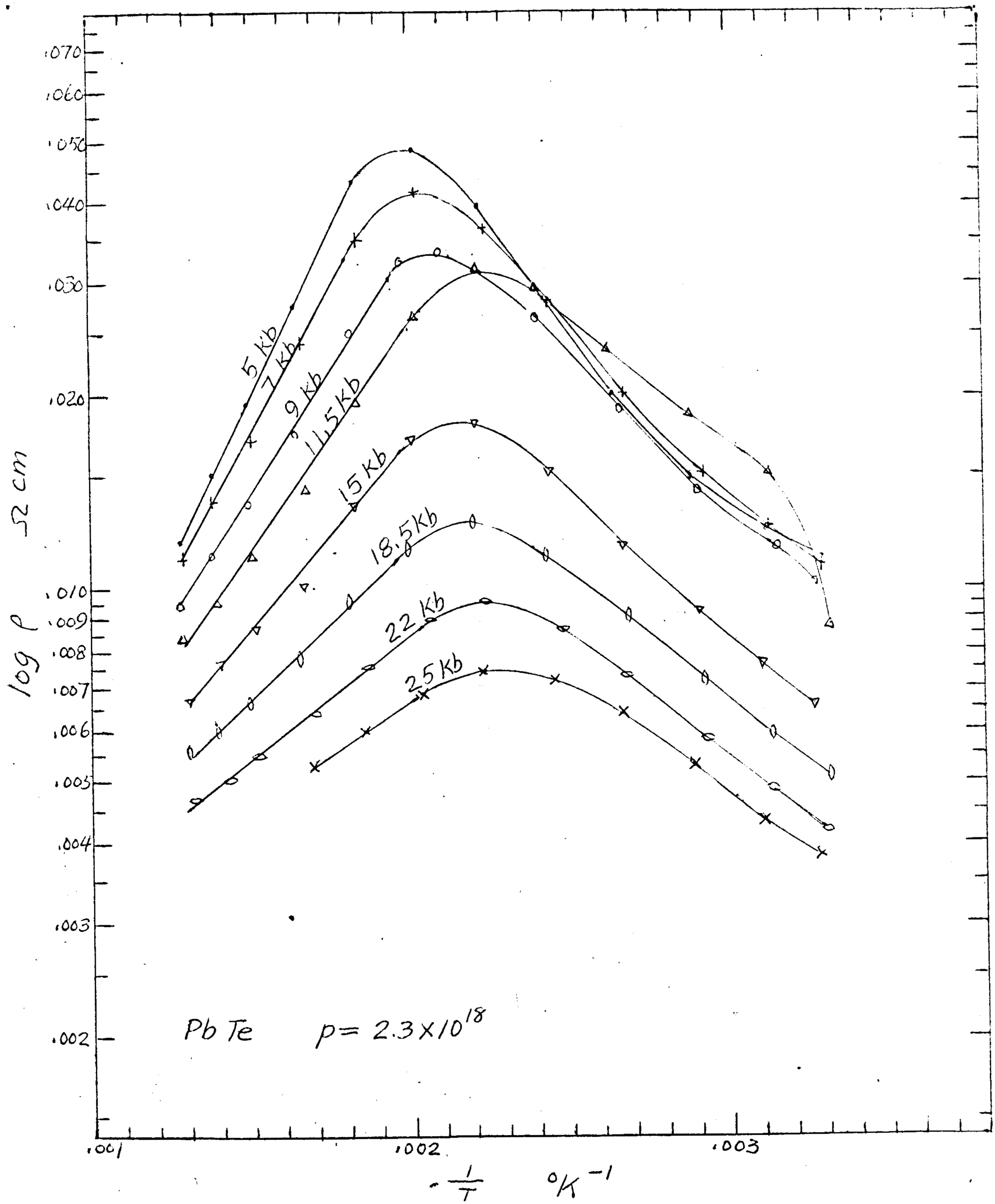

FIG. 1 log ρ vs $\frac{1}{T}$

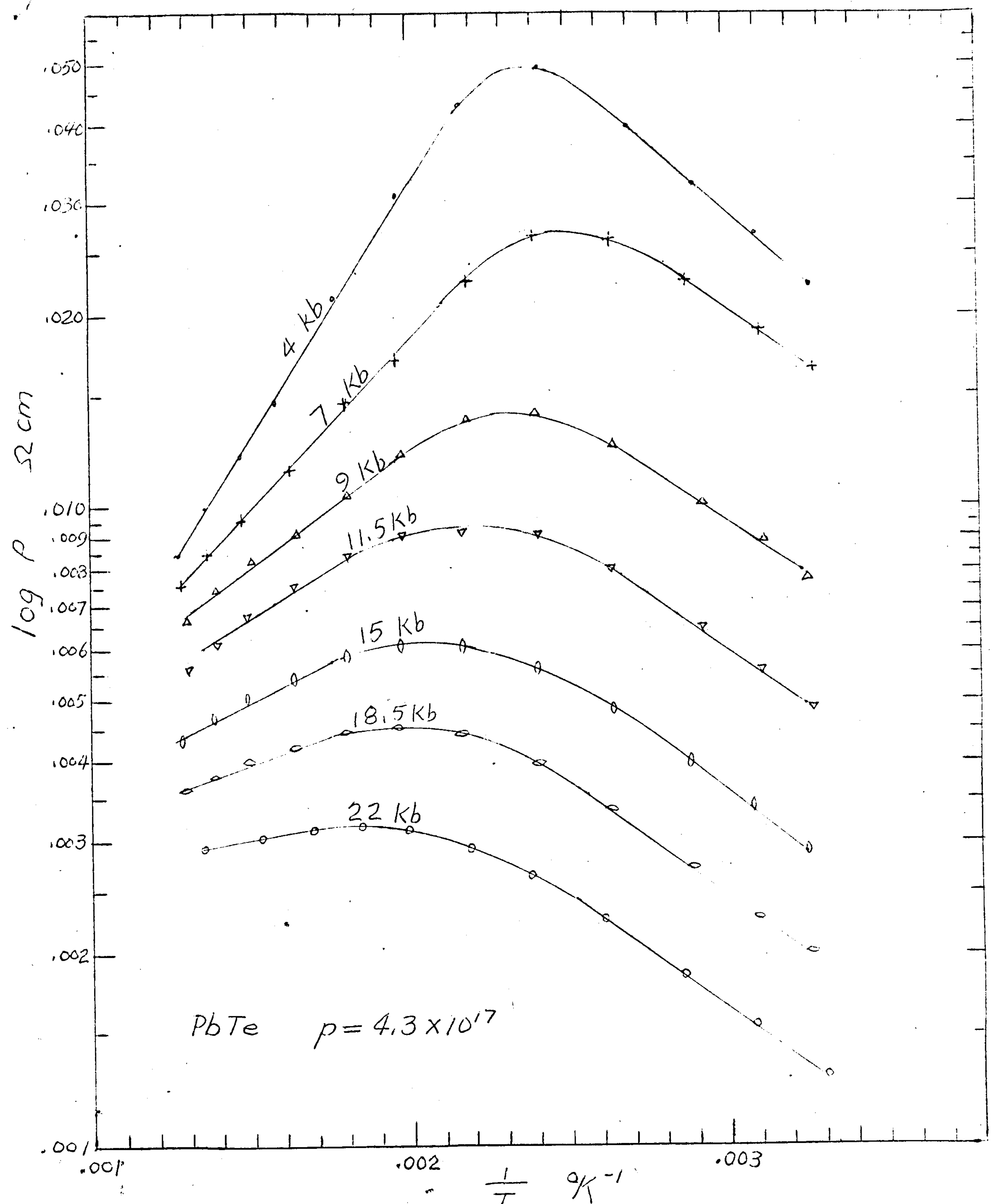

FIG. 2 log ρ vs $\frac{1}{T}$

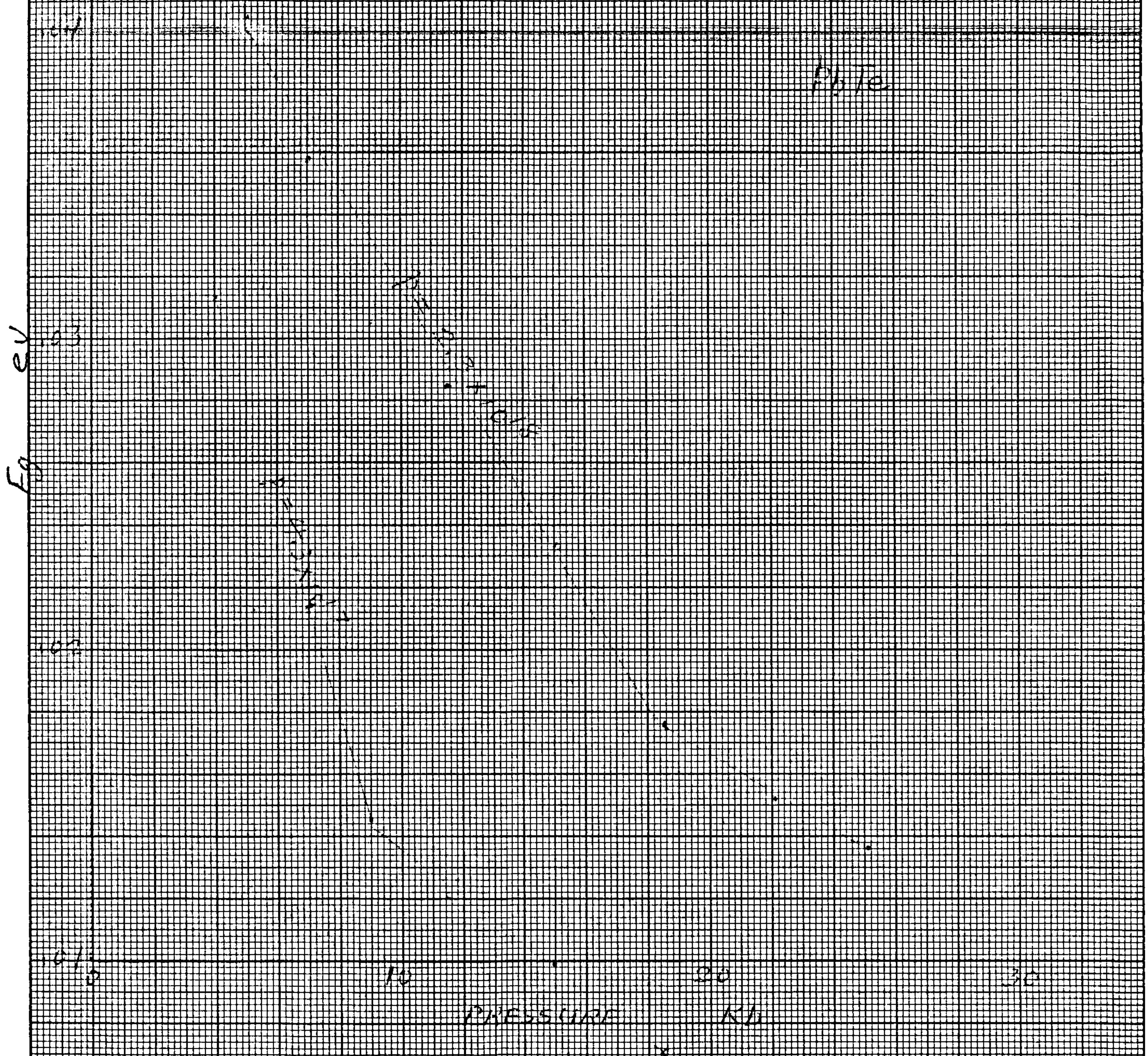

FIG. 3 Energy Gap VS Pressure

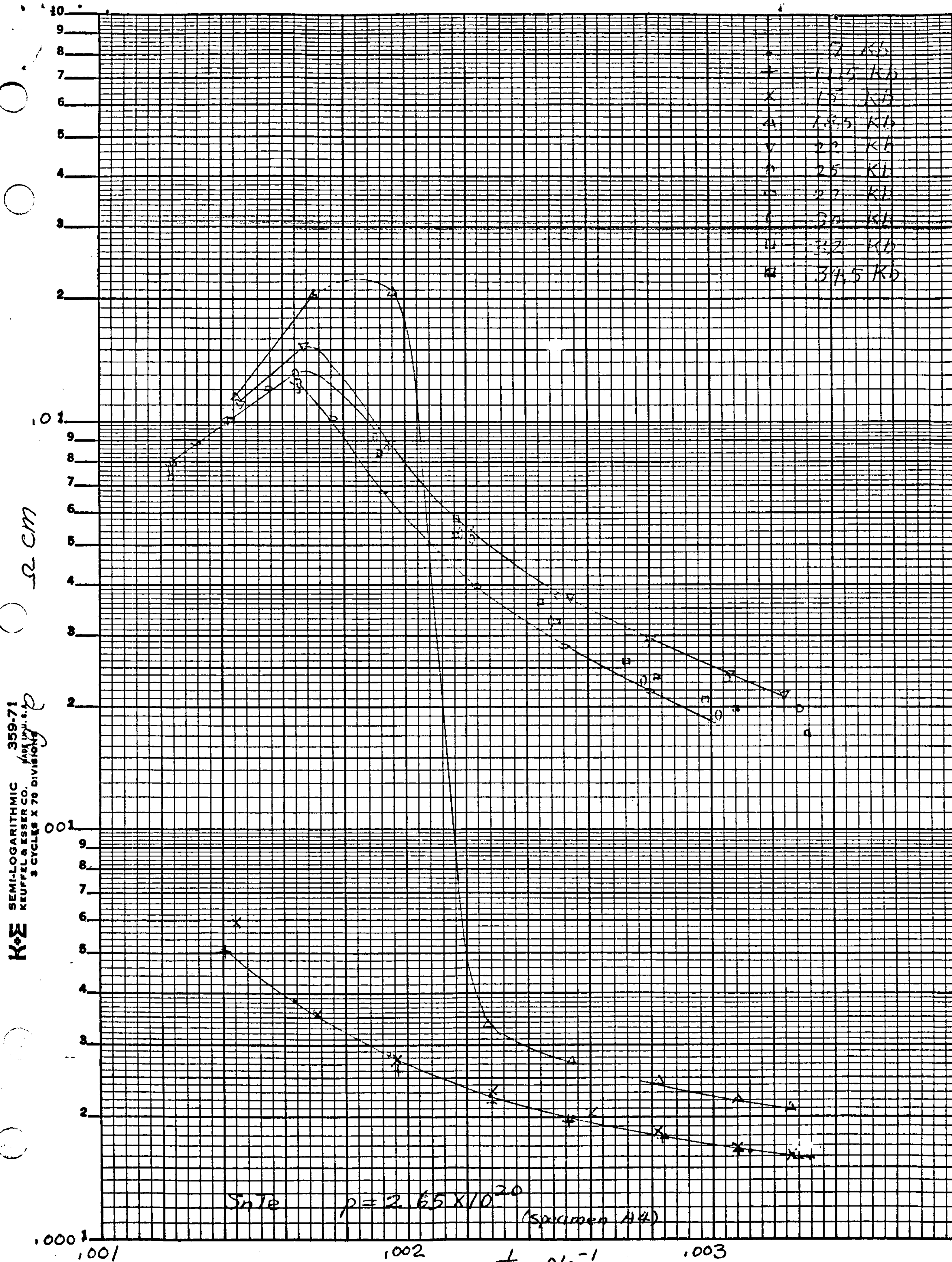

FIG. 4 log ρ vs 1/T

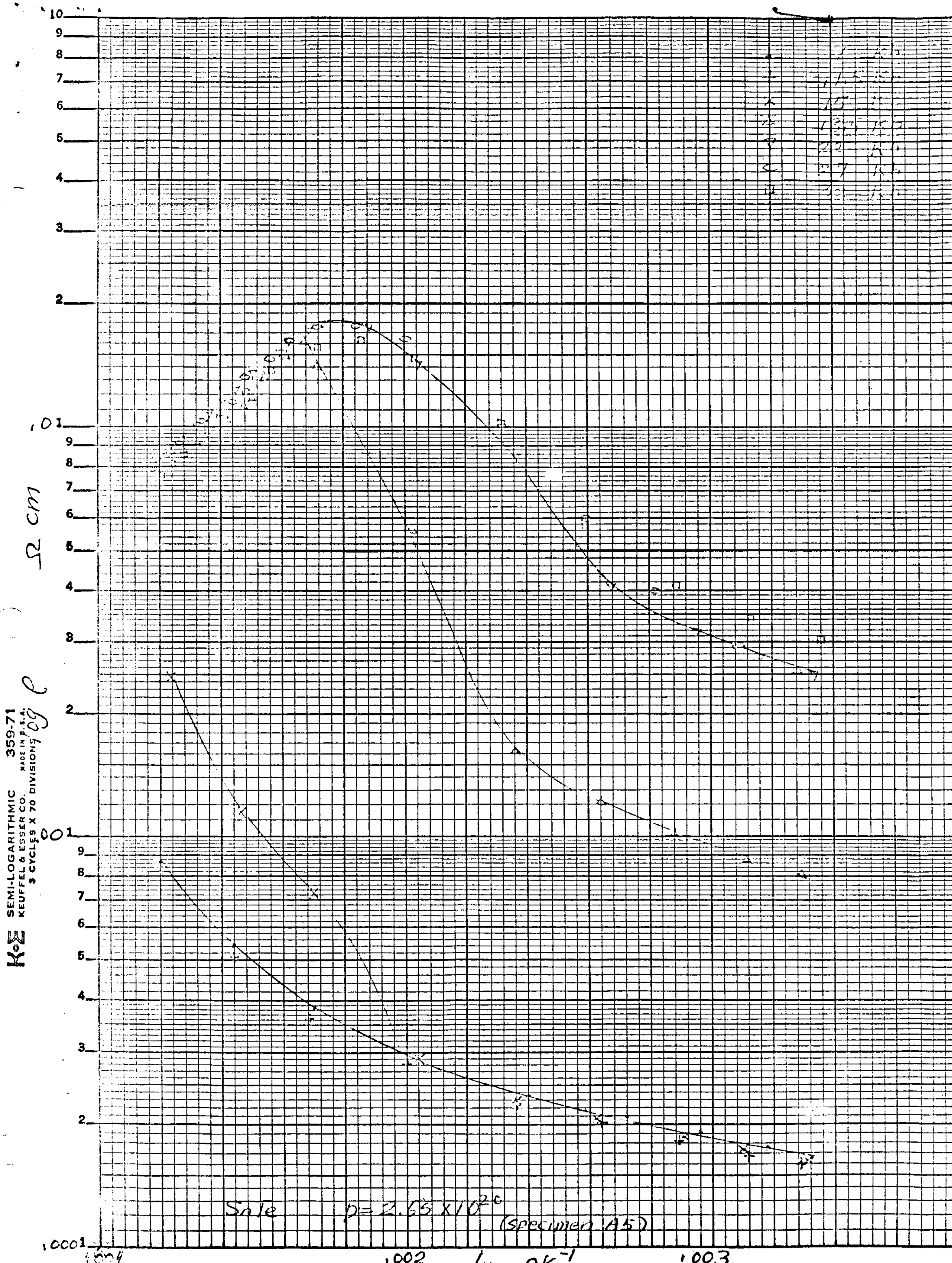

FIG. 5 log ρ vs 1/T

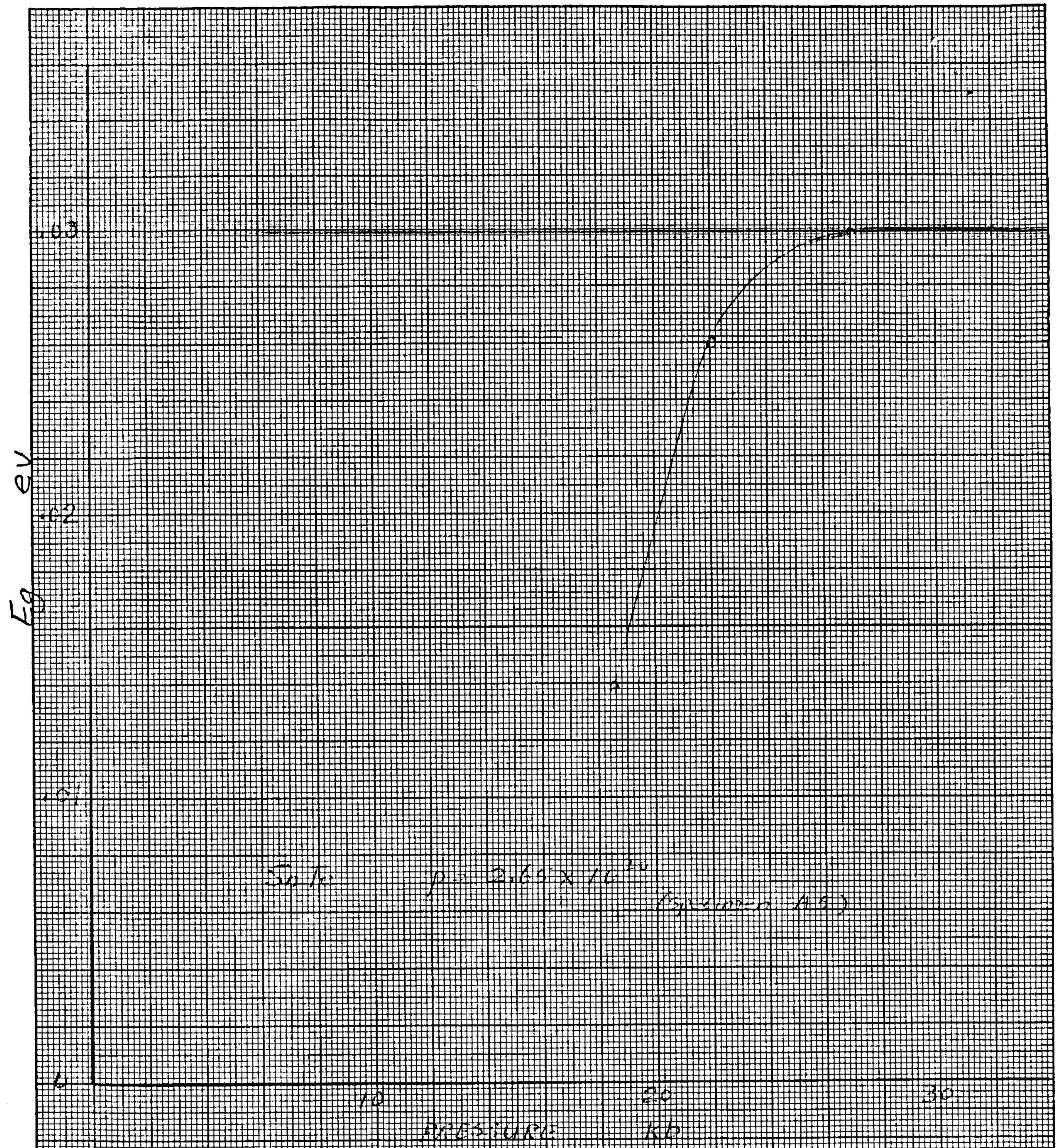

FIG. 6 Energy Gap vs Pressure